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(54) Titre : COMPOSITION DE POLYURETHANNE AUTO-ADHESIVE A FAIBLE TENEUR EN MONOMERE  
(54) Title: PRESSURE-SENSITIVE POLYURETHANE COMPOSITION WITH A LOW MONOMER CONTENT

(57) Abrégé/Abstract:

The invention relates to a polyurethane composition with the properties of a pressure-sensitive adhesive, to a method for its production and to its use as pressure-sensitive adhesive. The aim of the invention is to provide an optimized adhesive that has good adhesive properties even when the adhesive link has been repeatedly released and joined again and with a reduced migration of noxious components. To this end, the invention provides a polyurethane composition that is obtained by reacting two components A and B, wherein a) at least one polyurethane prepolymer A1 is used as component the A, said prepolymer having been obtained by reacting at least one polyol component with at least two bifunctional different isocyanates, and b) at least one bifunctional hardener as the component B, said hardener having per molecule at least two functional groups that are reactive to isocyanate groups. The ratio of isocyanate groups to functional groups that are reactive to isocyanate groups should be greater than 0.75 and lower than 1.15.

## Pressure-Sensitive Polyurethane Composition with a Low Monomer Content

This invention relates to a polyurethane composition with contact adhesive properties and a low monomer content, to processes for its production and to its use as a contact adhesive.

5 Foods are frequently marketed in portioned form in the interests of convenient handling and easier portioning by the consumer. Examples of portioned foods are sausage, cheese and ready-made salads which are packed in portioned form. The consumer merely has to open the pack, remove the required amount of food and then store the rest pending final consumption. However, problems arise out of the fact that corresponding  
10 packs are often not resealable. As a result, the food left in the pack dries out in storage, becomes unsightly and loses its typical taste.

Although there are already packs which can be resealed by mechanically engaging the cover in an encircling bead, such packs have the disadvantage that they are generally bulky, i.e. do not satisfy the  
15 commercial need for space-saving packs.

There are also packs where the cover is joined to the container part by an adhesive. However, packs such as these often have the disadvantage that the adhesive prevents resealing of the pack after it has been opened only once as a result of inadequate contact adhesive properties.

20 In addition, the adhesives in question are frequently applied from the melt. However, the melting temperatures of hitherto known contact adhesives which might otherwise be suitable for such packs are generally so high that packaging materials with a low melting or softening point cannot be treated with such adhesives. This means that the choice of  
25 packaging materials is limited which in turn places an unwanted restriction on the freedom to trade of corresponding manufacturers and packaging

factories. In addition, adhesives of the type in question are expected not to release any harmful substances into the packed food, i.e. not to cause any contamination of the food with harmful compounds present in the adhesive.

Isocyanate-terminated polyurethane prepolymers have been known  
5 for some time. They may readily be chain-extended or crosslinked with suitable hardeners, usually polyhydric alcohols, to form high molecular weight materials.

In order to obtain isocyanate-terminated polyurethane prepolymers, it is standard practice to react polyhydric alcohols with an excess of  
10 polyisocyanates, generally at least predominantly diisocyanates. Molecular weight can be controlled at least approximately through the ratio of OH groups to isocyanate groups. Whereas a ratio of OH groups to isocyanate groups of, or approaching, 1:1 leads to hard, possibly brittle molecules with high molecular weights, a statistical average of one diisocyanate molecule -  
15 where diisocyanates are used - is attached to each OH group where the OH : isocyanate group ratio is about 2:1, so that ideally no oligomerization or chain extension occurs in the course of the reaction.

In practice, however, chain-extending reactions are impossible to suppress with the result that, on completion of the reaction, a certain  
20 quantity of the component used in excess is left over irrespective of the reaction time. If diisocyanate, for example, is used as the excess component, a generally considerable proportion of this component remains behind in the reaction mixture for the reasons explained above.

The presence of such components is particularly problematical when  
25 they consist of readily volatile diisocyanates. The vapors of these diisocyanates are often harmful to the skin and the application of products with a high content of such readily volatile diisocyanates requires elaborate measures on the part of the user to protect the people involved in processing the product, more particularly elaborate measures for keeping  
30 the surrounding air clean to breathe.

Since protective measures and cleaning measures generally involve considerable expense, there is a need on the part of the user for products which have a low percentage content of readily volatile diisocyanates depending on the isocyanate used.

5 In the context of the present invention, "readily volatile" substances are understood to be substances which have a vapor pressure at around 30°C of more than about 0.0007 mmHg or a boiling point of less than about 190°C (70 mPa).

If low-volatility diisocyanates, more particularly the widely used  
10 bicyclic diisocyanates, for example diphenyl methane diisocyanates, are used instead of the readily volatile diisocyanates, polyurethane binders with a viscosity normally outside the range suitable for simple processing methods are generally obtained. In cases such as these, the viscosity of the polyurethane prepolymers can be reduced by adding suitable solvents  
15 although this is not consistent with the absence of solvents normally demanded. Another way of reducing viscosity without solvents is to add an excess of monomeric polyisocyanates which are incorporated in the coating or bond (reactive diluent) in the course of a subsequent curing/hardening process (after the addition of a hardener or by curing  
20 under the influence of moisture).

Whereas the viscosity of the polyurethane prepolymers can actually be reduced in this way, the generally incomplete reaction of the reactive diluent often leads to the presence in the bond or coating of free monomeric polyisocyanates which are capable of "migrating", for example  
25 within the coating or bond or, in some cases, even into the coated or bonded materials themselves. Corresponding constituents of a coating or bond are often referred to among experts as "migrates". By contact with moisture, the isocyanate groups of the migrates are continuously reacted to form amino groups. The aromatic amines normally formed in this way are  
30 suspected of having a carcinogenic effect. Accordingly, the migrates in

question are undesirable above all in the packaging field, especially in the packaging of foods.

DE-A 34 01 129 relates to a process for the production of mixed polyurethane prepolymers in which polyhydric alcohols are first reacted with the faster reacting isocyanate group of an asymmetrical diisocyanate, the more slowly reacting group being left intact, after which the reaction products are combined with a symmetrical diisocyanate of which the equally reactive isocyanate groups react more quickly than the slowly reacting groups of the first polyfunctional isocyanate compound mentioned. The described polyurethane prepolymers have high viscosities and hence high processing temperatures so that they can only be used under conditions which allow high processing temperatures.

Unfortunately, highly viscous polyurethane prepolymers of the type in question allow only a limited choice of materials to be bonded on account of their high processing temperature. In the case of adhesive-laminated laminates, delamination or dimensional changes often occur at the point of application when the hotmelt adhesive is applied at overly high temperature.

Accordingly, there was a need for solventless adhesives with contact adhesive properties which would guarantee a lower application temperature, would quickly lead to a firm adhesive bond, would be substantially free from migratable substances and would show satisfactory contact adhesive properties even after repeated opening and re-establishment of the adhesive bond.

There was also a need for packs which would allow compact packaging of the product to be packaged and at the same time would guarantee the required resealability, would not cause any contamination of the product to be packaged and in addition could consist of a variety of packaging materials.

Accordingly, the problem addressed by the invention was to provide

a contact adhesive polyurethane composition that would satisfy the requirements stated above.

Another problem addressed by the invention was to provide a pack that could easily be opened and closed by the user.

5       The problems stated above are solved by a polyurethane composition obtainable by reacting a polyurethane prepolymer containing NCO groups with a corresponding hardener containing OH groups and by packs obtainable using such a polyurethane composition.

10       Accordingly, the present invention relates to a polyurethane composition obtainable by reacting two components A and B,

- a) at least one polyurethane prepolymer A1 obtainable by reacting at least one polyol component with at least two at least difunctional different isocyanates being used as component A and
- b) an at least difunctional hardener containing at least two isocyanate-  
15       reactive functional groups per molecule being used as component B, and the ratio of isocyanate groups to isocyanate-reactive functional groups being greater than 0.75:1 and smaller than 1.15:1.

20       "Low viscosity" in the context of the present invention means a (Brookfield) viscosity at 70°C of less than 4,500 mPas, for example 3,500 mPas or lower.

25       In the context of the present specification, "functional groups reactive to isocyanate groups" are functional groups which are capable of reacting with urethane groups to form at least one covalent bond. Suitable reactive functional groups can be monofunctional in the context of a reaction with isocyanates, for example OH groups or mercapto groups. However, they may also be difunctional to isocyanates, for example amino groups. Accordingly, a molecule containing one amino group also has two isocyanate-reactive functional groups. It is not necessary in this connection for a single molecule to contain two separate isocyanate-reactive functional  
30       groups. What is important is that the molecule containing two isocyanate

groups is able to enter into a reaction to form a covalent bond.

Component A is a polyurethane prepolymer A1 containing two isocyanate groups or a mixture of two or more polyurethane prepolymers containing at least two isocyanate groups which is preferably obtainable by the reaction of a polyol component with an at least difunctional isocyanate. If two or more polyurethane prepolymers are present in component A1, there are collectively referred to as component A1 in the present specification.

In the context of the present invention, a "polyurethane prepolymer" is understood to be the compound which is obtained, for example, when a polyol component is reacted with at least two at least difunctional isocyanates. Accordingly, the expression "polyurethane prepolymer" encompasses both compounds of relatively low molecular weight, as formed for example in the reaction of a polyol with an excess of polyisocyanate, and also oligomeric or polymeric compounds. The expression "polyurethane prepolymer" also encompasses the compounds formed, for example, in the reaction of a trihydric or tetrahydric polyol with a molar excess of diisocyanates, based on the polyol. In this case, one molecule of the resulting compound carries several isocyanate groups.

Molecular weights relating to polymeric compounds represent the number average molecular weight ( $M_n$ ), unless otherwise indicated. All molecular weights are values obtainable by gel permeation chromatography (GPC), unless otherwise indicated.

In general, the polyurethane prepolymers used for the purposes of the present invention have a molecular weight in the range from about 500 to about 15,000 or in the range from about 500 to about 10,000, for example of the order of 5,000, but especially in the range from about 700 to about 4,500.

The polyurethane prepolymer containing at least two isocyanate groups or the mixture of polyurethane prepolymers containing two or more

but at least two isocyanate groups preferably has at least two differently attached types of isocyanate groups, of which at least one type has a lower reactivity to isocyanate-reactive groups than the other type or the other types of isocyanate groups. Isocyanate groups with a relatively low reactivity to isocyanate-reactive groups (by comparison with at least one other isocyanate group present in the polyurethane binder) are also referred to hereinafter as "less reactive isocyanate groups" while the corresponding isocyanate group with a higher reactivity to isocyanate-reactive compounds is also referred to as the "more reactive isocyanate group".

According to the present invention, therefore, a difunctional polyurethane prepolymer for example containing two differently attached isocyanate groups, one of the isocyanate groups having a higher reactivity to isocyanate-reactive groups than the other isocyanate group, may be used as component A. A polyurethane prepolymer such as this may be obtained, for example, from the reaction of an at least dihydric alcohol with compounds containing two different, for example difunctional, isocyanate groups. The ratio of OH groups to isocyanate groups in this reaction is at least about 0.55, for example about 0.55 to about 4:1. In a preferred embodiment of the invention, the reaction is carried out, for example, in such a way that, on average, each molecule of the dihydric alcohol reacts with one molecule of the compounds containing different isocyanate groups.

A trifunctional or higher polyurethane prepolymer may also be used as component A, in which case one molecule of the polyurethane prepolymer for example may contain a different number of less reactive and more reactive isocyanate groups.

In another preferred embodiment, mixtures of two or more different polyurethane prepolymers may be used as component A. The mixtures mentioned may be polyurethane prepolymers in which individual molecules



carry identically attached isocyanate groups. In this embodiment, at least one more reactive and one less reactive type of isocyanate group must be present in the mixture as a whole. Besides molecules containing one or more identically attached isocyanate groups, the mixture may also contain  
5 other molecules which carry both one or more identically attached isocyanate groups and one or more differently attached isocyanate groups.

In addition to polyurethane prepolymers, component A according to the invention preferably contains as component A2 an at least difunctional isocyanate of which the molecular weight is lower than the molecular  
10 weight of the polyurethane prepolymers A1 present in component A and of which the isocyanate groups have a higher reactivity to isocyanate-reactive compounds than the less reactive type of isocyanate groups present in component A1.

In general, component A2 has a molecular weight of up to about  
15 1,000, molecular weights of up to about 720 or lower, for example of the order of 550, 500, 450, 400 or lower, being preferred. Component A1 may consist, for example, of low molecular weight diisocyanates with a molecular weight of up to about 300 or of the reaction products of dihydric or higher alcohols with an at least equimolar quantity of such low molecular  
20 weight diisocyanates, based on the OH groups of the dihydric or higher alcohol. Also suitable as component A1 are, for example, the trimerization products of difunctional isocyanates, the isocyanurates.

The polyurethane binder according to the invention contains at most about 5% by weight of component A2, based on component A as a whole.

25 Component A according to the invention preferably has a content of readily volatile isocyanate-functional monomers of less than 2% by weight or less than 1% by weight or preferably less than 0.5% by weight. These limits apply in particular to readily volatile isocyanate compounds which have only a limited danger potential for people involved in their processing,  
30 for example to isophorone diisocyanate (IPDI), hexamethylene diiso-

cyanate (HDI), tetramethyl xylol diisocyanate (TMXDI) or cyclohexane diisocyanate. In the case of certain readily volatile isocyanate compounds, especially those which represent a serious risk to people involved in their processing, their content in the polyurethane binder according to the invention is preferably less than 0.3% by weight and more preferably less than 0.1% by weight. These particular isocyanate compounds include, above all, toluene diisocyanate (TDI). In another preferred embodiment of the invention, the polyurethane binder has a TDI and HDI content of less than 0.05% by weight.

10 In one preferred embodiment of the invention, the polyurethane binder according to the invention may contain an at least trifunctional isocyanate as component A3 in addition to components A1 and A2.

Suitable at least trifunctional isocyanates are, for example, the trimerization and oligomerization products of the above-mentioned polyisocyanates which can be obtained by suitably reacting polyisocyanates, preferably diisocyanates, to form isocyanurate rings. If oligomerization products are used, those which have a degree of oligomerization of on average about 3 to about 5 are particularly suitable.

Isocyanates suitable for the production of trimers are the diisocyanates mentioned above, the trimerization products of the isocyanates HDI, MDI or IPDI being particularly preferred.

Polymeric isocyanates obtained, for example, as residue in the distillation of diisocyanates are also suitable for use as component A2. The polymeric MDI obtainable from the distillation residue in the distillation of MDI is particularly suitable.

25 In one preferred embodiment of the invention, Desmodur N 3300, Desmodur N 100, the IPDI-trimeric isocyanurate T 1890 (products of Bayer AG) or triphenyl methane triisocyanate, for example, is used as component A3.

30 Component A3 is preferably used in a quantity of at most about 1 to

about 10% by weight, for example in quantity of about 2 to about 7% by weight or in a quantity of about 3 to about 5% by weight as a constituent of component A.

5 In one preferred embodiment of the invention, component A is prepared by an at least two-stage reaction in which

(c) in a first stage, a polyurethane prepolymer is prepared from an at least difunctional isocyanate and at least a first polyol component, the NCO:OH ratio being smaller than 2 and free OH groups still  
10 being present in the polyurethane prepolymer,

and

(d) in a second stage, another at least difunctional isocyanate is reacted with the polyurethane prepolymer from the first stage,

15 the isocyanate groups of the isocyanate added in the second stage having a higher reactivity to isocyanate-reactive compounds than at least the predominant percentage of the isocyanate groups present in the polyurethane prepolymer from the first stage.

In another preferred embodiment, the other at least difunctional  
20 isocyanate is added in excess, based on free OH groups of component A, the non-OH-reactive part of the other at least difunctional isocyanate representing component A2.

In another preferred embodiment, component A is prepared by an at least two-stage reaction in which

25 (e) in a first stage, a polyurethane prepolymer is prepared from an at least difunctional isocyanate and at least a first polyol component, the NCO:OH ratio being smaller than 2 and free OH groups still being present in the polyurethane prepolymer,

and

30 (f) in a second stage, another at least difunctional isocyanate and another

polyol component are reacted with the polyurethane prepolymer from the first stage,

the isocyanate groups of the isocyanate added in the second stage having a higher reactivity to isocyanate-reactive compounds than at least the predominant percentage of the isocyanate groups present in the polyurethane prepolymer from the first stage.

In another preferred embodiment, the other at least difunctional isocyanate is added in excess, based on free OH groups of component A and the other polyol component, the non-OH-reactive part of the other at least difunctional isocyanate representing component A2.

According to the invention, the OH:NCO ratio in the production of component A in the second stage is preferably about 1 to about 15, for example about 1.5 to about 12:1.

In one preferred embodiment of the invention, the OH:NCO ratio in the second stage is about 1 to about 2.

In another preferred embodiment of the invention, the OH:NCO ratio in the first stage is about 0.55 to about 4 and more particularly about 0.6 to about 3:1, the described ratios optionally being maintained for the second stage also.

In the context of the present invention, the expression "polyol component" encompasses a single polyol or a mixture of two or more polyols which may be used for the production of polyurethanes. A polyol is understood to be a polyhydric alcohol, i.e. a compound containing more than one OH group in the molecule.

Various polyols may be used as the polyol component for the production of component A. They include, for example, aliphatic alcohols containing 2 to 4 OH groups per molecule. The OH groups may be both primary and secondary. Suitable aliphatic alcohols include, for example, ethylene glycol, propylene glycol, butane-1,4-diol, pentane-1,5-diol,

hexane-1,6-diol, heptane-1,7-diol, octane-1,8-diol and higher homologs or isomers thereof which the expert can obtain by extending the hydrocarbon chain by one  $\text{CH}_2$  group at a time or by introducing branches into the carbon chain. Also suitable are higher alcohols such as, for example, glycerol, trimethylol propane, pentaerythritol and oligomeric ethers of the substances mentioned either individually or in the form of mixtures of two or more of the ethers mentioned with one another.

Other suitable polyol components for the production of component A are the reaction products of low molecular weight polyhydric alcohols with alkylene oxides, so-called polyethers. The alkylene oxides preferably contain 2 to 4 carbon atoms. Suitable reaction products of the type in question are, for example, the reaction products of ethylene glycol, propylene glycol, the isomeric butane diols or hexane diols with ethylene oxide, propylene oxide or butylene oxide or mixtures of two or more thereof. The reaction products of polyhydric alcohols, such as glycerol, trimethylol ethane or trimethylol propane, pentaerythritol or sugar alcohols or mixtures of two or more thereof, with the alkylene oxides mentioned to form polyether polyols are also suitable. Polyether polyols with a molecular weight of about 100 to about 10,000 and preferably in the range from about 200 to about 5,000 are particularly suitable. According to the invention, polypropylene glycol with a molecular weight of about 300 to about 2,500 is most particularly preferred. Other suitable polyol components for the production of component A are polyether polyols as obtained, for example, from the polymerization of tetrahydrofuran.

The polyethers are reacted in known manner by reacting the starting compound containing a reactive hydrogen atom with alkylene oxides, for example ethylene oxide, propylene oxide, butylene oxide, styrene oxide, tetrahydrofuran or epichlorohydrin or mixtures of two or more thereof.

Suitable starting compounds are, for example, water, ethylene glycol, 1,2- or 1,3-propylene glycol, 1,4- or 1,3-butylene glycol, hexane-1,6-

diol, octane-1,8-diol, neopentyl glycol, 1,4-hydroxymethyl cyclohexane, 2-methyl propane-1,3-diol, glycerol, trimethylol propane, hexane-1,2,6-triol, butane-1,2,4-triol, trimethylol ethane, pentaerythritol, mannitol, sorbitol, methyl glycosides, sugars, phenol, isononylphenol, resorcinol, hydroquinone, 1,2,2- or 1,1,2-tris-(hydroxyphenyl)-ethane, ammonia, methyl amine, ethylenediamine, tetra- or hexamethylenediamine, triethanolamine, aniline, phenylenediamine, 2,4- and 2,6-diaminotoluene and polyphenylpolymethylene polyamines, which may be obtained by aniline/formaldehyde condensation, or mixtures of two or more thereof.

10 Polyethers modified by vinyl polymers are also suitable for use as a polyol component. Products such as these can be obtained, for example, by polymerizing styrene or acrylonitrile or mixtures thereof in the presence of polyethers.

Other suitable polyol components for the production of component A  
15 are polyester polyols with a molecular weight of about 200 to about 10,000. For example, it is possible to use polyester polyols obtained by reacting low molecular weight alcohols, more particularly ethylene glycol, diethylene glycol, neopentyl glycol, hexanediol, butanediol, propylene glycol, glycerol or trimethylol propane, with caprolactone. Other suitable polyhydric  
20 alcohols for the production of polyester polyols are 1,4-hydroxymethyl cyclohexane, 2-methyl propane-1,3-diol, butane-1,2,4-triol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol and polybutylene glycol.

Other suitable polyester polyols can be obtained by poly-  
25 condensation. Thus, dihydric and/or trihydric alcohols may be condensed with less than the equivalent quantity of dicarboxylic acids and/or tricarboxylic acids or reactive derivatives thereof to form polyester polyols. Suitable dicarboxylic acids are, for example, adipic acid or succinic acid and higher homologs thereof containing up to 16 carbon atoms,  
30 unsaturated dicarboxylic acids, such as maleic acid or fumaric acid, and

aromatic dicarboxylic acids, more particularly the isomeric phthalic acids, such as phthalic acid, isophthalic acid or ter phthalic acid. Citric acid and trimellitic acid, for example, are also suitable tricarboxylic acids. The acids mentioned may be used individually or as mixtures of two or more thereof.

- 5 Polyester polyols of at least one of the dicarboxylic acids mentioned and glycerol which have a residual content of OH groups are particularly suitable for the purposes of the present invention. Particularly suitable alcohols are hexanediol, ethylene glycol, diethylene glycol or neopentyl glycol or mixtures of two or more thereof. Particularly suitable acids are
- 10 isophthalic acid and adipic acid and mixtures thereof.

In a particularly preferred embodiment of the invention, polyols used as polyol component for the production of component A are, for example, dipropylene glycol and/or polypropylene glycol with a molecular weight of about 400 to about 2,500 and polyester polyols, preferably polyester

15 polyols obtainable by polycondensation of hexanediol, ethylene glycol, diethylene glycol or neopentyl glycol or mixtures of two or more thereof and isophthalic acid or adipic acid or mixtures thereof.

High molecular weight polyester polyols include, for example, the reaction products of polyhydric, preferably dihydric, alcohols (optionally

20 together with small quantities of trihydric alcohols) and polybasic, preferably dibasic, carboxylic acids. Instead of free polycarboxylic acids, the corresponding polycarboxylic anhydrides or corresponding polycarboxylic acid esters with alcohols preferably containing 1 to 3 carbon atoms may also be used (where possible). The polycarboxylic acids may be

25 aliphatic, cycloaliphatic, aromatic or heterocyclic or both. They may optionally be substituted, for example by alkyl groups, alkenyl groups, ether groups or halogens. Suitable polycarboxylic acids are, for example, succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, phthalic anhydride,

30 tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachloro-

phthalic anhydride, endomethylene tetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, dimer fatty acid or trimer fatty acid or mixtures of two or more thereof. Small quantities of monofunctional fatty acids may optionally be present in the reaction mixture.

The polyesters may optionally contain a small percentage of terminal carboxyl groups. Polyesters obtainable from lactones, for example  $\epsilon$ -caprolactone, or hydroxycarboxylic acids, for example  $\omega$ -hydroxycaproic acid, may also be used.

Polyacetals are also suitable polyol components. Polyacetals are compounds which can be obtained from glycols, for example diethylene glycol or hexanediol or mixtures thereof with formaldehyde. Polyacetals suitable for use in accordance with the invention may also be obtained by the polymerization of cyclic acetals.

Other suitable polyols for the production of components A are polycarbonates. Polycarbonates may be obtained, for example, by the reaction of diols, such as propylene glycol, butane-1,4-diol or hexane-1,6-diol, diethylene glycol, triethylene glycol or tetraethylene glycol or mixtures of two or more thereof, with diaryl carbonates, for example diphenyl carbonate, or phosgene.

OH-functional polyacrylates are also suitable polyol components for the production of component A. These polyacrylates are obtainable, for example, by the polymerization of ethylenically unsaturated monomers containing an OH group. Monomers such as these are obtainable, for example, by the esterification of ethylenically unsaturated carboxylic acids and dihydric alcohols, the alcohol generally being present in a slight excess. Ethylenically unsaturated carboxylic acids suitable for this purpose are, for example, acrylic acid, methacrylic acid, crotonic acid or maleic acid. Corresponding OH-functional esters are, for example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-



hydroxypropyl methacrylate, 3-hydroxypropyl acrylate or 3-hydroxypropyl methacrylate or mixtures of two or more thereof.

Polyols suitable for the production of component A may have an OH value of about 90 to about 300, for example of about 100 to about 260 or  
5 about 130 to about 250.

To produce component A as a whole, the corresponding polyol component is reacted with an at least difunctional isocyanate. Suitable at least difunctional isocyanates for the production of component A are basically any isocyanates containing at least two isocyanate groups  
10 although, in general, compounds containing 2 to 4 isocyanate groups, more particularly 2 isocyanate groups, are preferred for the purposes of the present invention.

At least difunctional isocyanates suitable as the at least difunctional isocyanate for the production of component A are described in the  
15 following.

These at least difunctional isocyanates are, for example, ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate and mixtures of two or more thereof, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate, IPDI),  
20 2,4- and 2,6-hexahydrotoluene diisocyanate, tetramethyl xylylene diisocyanate (TMXDI), 1,3- and 1,4-phenylene diisocyanate, 2,4- or 2,6-toluene diisocyanate (TDI), diphenyl methane-2,4'-diisocyanate, diphenylmethane-2,2'- diisocyanate or diphenylmethane-4,4'-diisocyanate (isocyanates of the  
25 MDI series) or mixtures of two or more of the diisocyanates mentioned.

According to the invention, other suitable isocyanates for the production of component A are trifunctional or higher isocyanates obtainable, for example, by oligomerization of diisocyanates. Examples of such trifunctional and higher polyisocyanates are the triisocyanurates of  
30 HDI or IPDI or mixtures thereof or mixed triisocyanurates thereof.

In one preferred embodiment of the invention, diisocyanates containing two isocyanate groups differing in their reactivity are used for the production of component A. Examples of such diisocyanates are 2,4- and 2,6-toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI). With  
5 non-symmetrical diisocyanates such as these, one isocyanate group generally reacts far more quickly with isocyanate-reactive groups, for example OH groups, while the remaining isocyanate group reacts comparatively sluggishly. Accordingly, in one preferred embodiment, a monocyclic non-symmetrical diisocyanate containing two isocyanate  
10 groups differing in their reactivity, as described above, is used for the production of component A.

In one particularly preferred embodiment, 2,4- or 2,6-toluene diisocyanate (TDI) or a mixture of the two isomers, but especially pure 2,4-TDI, is used for the production of component A.

15 Component B is produced using an at least difunctional isocyanate which ensures that at least the predominant percentage of the isocyanate groups of component B remaining after the reaction with the polyol component is more reactive than the predominant percentage of the isocyanate groups present in component A. Difunctional isocyanates of which the  
20 isocyanate groups are largely identical in their reactivity are preferably used for the production of component B. More particularly, these difunctional isocyanates are the symmetrical isocyanates, preferably the symmetrical, aromatic difunctional isocyanates. In one particularly preferred embodiment, the bicyclic, aromatic, symmetrical diisocyanates of the diphenyl  
25 methane series, more particularly MDI, are used for the production of component B.

A polyurethane composition with the advantages according to the invention can be produced in basically any way. However, two processes which are described hereinafter have proved to be particularly  
30 advantageous.

For example, the polyurethane binder can be directly produced by preparing component A and subsequently adding component A1.

However, the compound required as component A2 may actually be used in the preparation of component A and may be added in such an excess that the required final content of component A2 is reached.

Accordingly, component A may be produced, for example, by a two-stage process in which

(c) in a first stage, a first reaction product is prepared from an at least difunctional isocyanate and at least one polyol component and

(d) in a second stage, another at least difunctional isocyanate or another at least difunctional isocyanate and another polyol component is/are reacted in the presence of the first reaction product,

the predominant percentage of the isocyanate groups present on completion of the first stage having a lower reactivity to isocyanate-reactive groups, more particularly to OH groups, than the isocyanate groups of the at least difunctional isocyanate added in the second stage. In a preferred embodiment of the invention, the OH:NCO ratio in the second stage is about 0.2 to about 0.8:1.

In principle, any of the polyol components which have already been mentioned herein may be used as the other polyol component.

In one advantageous embodiment, the OH:NCO ratio in the first stage of the process according to the invention is less than 1:1. In one preferred embodiment, the ratio of OH groups to isocyanate groups in the first stage is about 0.4 to about 0.7:1 and, more particularly, more than 0.5 to about 0.7:1.

The reaction of a polyol component with the at least difunctional isocyanate in a first stage may be carried out in any manner known to the

expert under the general rules for producing polyurethanes. For example, the reaction may be carried out in the presence of solvents. Suitable solvents are, basically, any of the solvents typically used in polyurethan chemistry, more particularly esters, ketones, halogenated hydrocarbons, alkanes, alkenes and aromatic hydrocarbons. Examples of such solvents are methylene chloride, trichloroethylene, toluene, xylene, butyl acetate, amyl acetate, isobutyl acetate, methyl isobutyl ketone, methoxybutyl acetate, cyclohexane, cyclohexanone, dichlorobenzene, diethyl ketone, diisobutyl ketone, dioxane, ethyl acetate, ethylene glycol monobutyl ether acetate, ethylene glycol monoethyl acetate, 2-ethylhexyl acetate, glycol diacetate, heptane, hexane, isobutyl acetate, isooctane, isopropyl acetate, methyl ethyl ketone, tetrahydrofuran or tetrachloroethylene or mixtures of two or more of the solvents mentioned.

If the reaction components themselves are liquid or if at least one or more of the reaction components form(s) a solution or dispersion of other insufficiently liquid reaction components, there is no need at all to use solvents. A solventless reaction represents a preferred embodiment of the invention.

To carry out the first stage of the process according to the invention, the polyol is introduced into a suitable vessel, optionally together with a suitable solvent, and mixed. The at least difunctional isocyanate is then added with continued mixing. To accelerate the reaction, the temperature is normally increased. In general, the reaction mixture is heated to about 40 to about 80°C. The exothermic reaction which then begins provides for an increase in the temperature. The temperature of the mixture is kept at about 70 to about 110°C, for example at about 85 to 95°C or, more particularly, at about 75 to about 85°C, the temperature optionally being adjusted by suitable external measures, for example heating or cooling.

Catalysts typically used in polyurethane chemistry may optionally be added to the reaction mixture to accelerate the reaction. Dibutyl tin

dilaurate or diazabicyclooctane (DABCO) is preferably added. If it is desired to use a catalyst, the catalyst is generally added to the reaction mixture in a quantity of about 0.005% by weight or about 0.01% by weight to about 0.2% by weight, based on the mixture as a whole.

5        The reaction time for the first stage depends upon the polyol component used, upon the at least difunctional isocyanate used, upon the reaction temperature and upon the catalyst present, if any. The total reaction time is normally about 30 minutes to about 20 hours.

10        Isophorone diisocyanate (IPDI), tetramethylene xylene diisocyanate (TMXDI), hydrogenated diphenyl methane diisocyanate (MDI<sub>H12</sub>) or toluene diisocyanate (TDI) or a mixture of two or more thereof is preferably used as the at least difunctional isocyanate in the first stage.

15        To carry out the second stage of the process according to the invention, at least one other at least difunctional isocyanate is reacted with another polyol component or with a mixture of two or more other polyol components in admixture with component A obtained in the first stage. Any polyol from the group of polyols listed in the foregoing or a mixture of two or more thereof may be used as a constituent of the other polyol component or the mixture of two or more other polyol components. However, a  
20        polypropylene glycol with a molecular weight of about 400 to about 2500 or a polyester polyol with at least a high percentage and, more particularly, a predominant percentage of aliphatic dicarboxylic acids or a mixture of these polyols is preferably used as the polyol component in the second stage of the process according to the invention.

25        At least one polyisocyanate of which the isocyanate groups have a higher reactivity than the majority of the isocyanate groups present in the prepolymer is used as the at least difunctional isocyanate in the second stage of the process according to the invention. In other words, reactive isocyanate groups emanating from the at least difunctional isocyanate  
30        originally used for the production of component A may be present in the

prepolymer, the only requirement in this connection being that the predominant percentage of the isocyanate groups present in component A should have a lower reactivity than the isocyanate groups of the other at least difunctional isocyanate A1 optionally added in the second stage of the process according to the invention.

A bicyclic aromatic symmetrical diisocyanate is preferably used as the other at least difunctional isocyanate. The bicyclic isocyanates include, for example, diisocyanates of the diphenyl methane series, more particularly 2,2'-diphenyl methane diisocyanate, 2,4'-diphenyl methane diisocyanate and 4,4'-diphenyl methane diisocyanate. Of the diisocyanates mentioned, diphenyl methane diisocyanate, more particularly 4,4'-diphenyl methane diisocyanate, is particularly preferred as the other at least difunctional isocyanate for the second stage of the process according to the invention.

The other at least difunctional isocyanate is used in the second stage in a quantity of about 0.1 to about 5% by weight and preferably in a quantity of about 1 to about 3% by weight, based on the total quantity of component A.

In another preferred embodiment of the invention, component A1 is added in such a quantity that component A as a whole contains from about 2 to about 8% by weight, for example from about 3.5 to about 6.5% by weight, of isocyanate groups.

However, component A according to the invention can also be produced by mixing individual components C, D and E. In this process,

- (e) an isocyanate-functional polyurethane prepolymer obtainable by reacting a polyol component with an at least difunctional isocyanate is used as component C,
- (f) another isocyanate-functional polyurethane prepolymer obtainable by reacting a polyol component with another at least difunctional

isocyanate, of which the isocyanate groups have a higher reactivity to isocyanate-reactive groups than the isocyanate groups of component C, is used as component D

and

- 5 (g) another at least difunctional isocyanate, of which the molecular weight is lower than that of components C and D and of which the isocyanate groups have a higher reactivity to isocyanate-reactive groups than the isocyanate groups of component C, is used as component E,

10 the quantity of component E being gauged so that, on completion of mixing and after all the reactions, if any, taking place between components C, D and E have ended, about 2 to about 8% by weight and more particularly about 3.5 to about 6.5% by weight of component E is present in the polyurethane binder.

15 In the context of the present invention, the expression "all the reactions, if any, taking place between components C, D and E" refers to reactions of isocyanate groups with functional groups containing isocyanate-reactive hydrogen atoms. The addition of component E, particularly when components C or D or C and D, for example, contain free  
20 OH groups, generally leads to a reaction of the isocyanate groups of component E with the free OH groups. This results in a reduction in the content of component E. Accordingly, if reactions capable of leading to a reduction in the proportion of component E are likely to occur, component E must be added in such a quantity that, after all these reactions have ended,  
25 the required minimum quantity of component E is present in the polyurethane binder.

Any of the polyols described above and mixtures of two or more of the polyols mentioned may be used as the polyol component for the production of components C and D in the process according to the  
30 invention. The polyol components in particular mentioned in the present

specification as particularly suitable for the production of component A are also preferably used in the process according to the invention.

5 The foregoing observations on component A2 apply similarly to the at least difunctional isocyanate to be used as component E, of which the molecular weight is lower than that of components C and D and of which the isocyanate groups have a higher reactivity than the isocyanate groups of component C.

10 In one preferred embodiment of the invention, another at least trifunctional isocyanate may be added as component F after the two stages already described. Suitable at least trifunctional isocyanates are the polyisocyanates containing at least three NCO groups described in the foregoing or the trimerization and polymerization products of the difunctional isocyanates mentioned above.

15 Component A according to the invention and the polyurethane compositions produced therefrom in accordance with the invention are distinguished in particular by the fact that they have an extremely low content of readily volatile monomers containing isocyanate groups which is less than 2% by weight or less than 1% by weight, less than 0.5% by weight and, more particularly, less than about 0.1% by weight. It is 20 particularly emphasized in this connection that the process according to the invention does not require any separate process steps for removing readily volatile diisocyanate components.

To produce the polyurethane composition according to the invention, a hardener is used as component B in addition to component A.

25 A compound containing at least two functional groups reactive to the isocyanate groups of component A is preferably used as component B. In a preferred embodiment of the invention, the compounds used in component B have a molecular weight of up to 2,500. The functional groups reactive to the isocyanate groups of component F may be selected 30 in particular from amino groups, mercapto groups or OH groups.



Compounds suitable for use in component B may contain amino groups, mercapto groups or OH groups either individually or in admixture as long as the functionality requirement is fulfilled.

5 The OH value of the polyols used as component B is about 90 to about 350, for example about 100 to about 300, for example about 130 to about 250.

10 The functionality of the compounds suitable for use in component B is generally at least about two. Component B optionally has a percentage of compounds with a higher functionality, for example with a functionality of three, four or more. The total (average) functionality of component G is for example about two (for example when only difunctional compounds are used as component B) or more, for example about 2.1, 2.2, 2.5, 2.7 or 3. In another embodiment of the invention, component B has a functionality of about 2.0 to about 2.1, for example about 2.01, 2.03, 2.05, 2.07 or 2.09.

15 Component B preferably contains a polyol carrying at least two OH groups. Any of the polyols mentioned in the foregoing are suitable for use in component B providing they satisfy the limiting criterion of the upper molecular weight limit.

20 In a preferred embodiment of the present invention, a mixture of two or more polyols is used as component B, the mixture containing at least one polyester. In another preferred embodiment, a mixture containing at least one polyether is used as component B. In another preferred embodiment of the invention, a mixture containing at least one polyester, at least one difunctional polyether and at least one trifunctional polyether is used as component B.

25 In another preferred embodiment of the invention, a mixture of 0 to 80% by weight polyester, 0 to 10% by weight trifunctional polyether, 10 to 80% by weight difunctional polyether with a molecular weight ( $M_w$ ) of at least about 1,000 and 10 to 80% by weight difunctional polyether with a molecular weight ( $M_w$ ) of at most about 800 is used as component B.

According to the invention, component B is used in such a quantity that the ratio of isocyanate groups in component A to functional groups reactive to isocyanate groups of component A in component B is greater than about 0.75 and smaller than about 1.15. In another embodiment of the invention, the ratio is more than about 1 to about 1.15:1 and more particularly about 1.01 to about 1.1:1.

The polyurethane composition according to the invention generally has a viscosity of about 1,000 to about 5,000 mPas and more particularly of about 1,500 to about 3,000 mPas (Brookfield RVT D, spindle 27, 70°C), as measured immediately after components A and B have been mixed.

The polyurethane composition according to the invention may optionally contain additives. The additives may make up about 10% by weight of the composition as a whole.

Additives suitable for use in accordance with the present invention include, for example, plasticizers, stabilizers, antioxidants, dyes, photostabilizers and fillers.

Suitable plasticizers are, for example, plasticizers based on phthalic acid, more particularly dialkyl phthalates, phthalic acid esters esterified with a linear alkanol containing about 6 to about 12 carbon atoms representing preferred plasticizers. Dioctyl phthalate is particularly preferred.

Other suitable plasticizers are benzoate plasticizers, for example sucrose benzoate, diethylene glycol dibenzoate and/or diethylene glycol benzoate, in which about 50 to about 95% of all the hydroxyl groups have been esterified, phosphate plasticizers, for example t-butylphenyl diphenyl phosphate, polyethylene glycols and derivatives thereof, for example, diphenyl ethers of poly(ethylene glycol), liquid resin derivatives, for example the methyl ester of hydrogenated resin, vegetable and animal oils, for example glycerol esters of fatty acids and polymerization products thereof.

Stabilizers or antioxidants suitable for use as additives in

accordance with the invention include hindered phenols of high molecular weight ( $M_n$ ), polyhydric phenols and sulfur- and phosphorus-containing phenols. Phenols suitable for use as additives in accordance with the invention are, for example, 1,3,5-trimethyl-2,4,6-tris-(3,5-ditert.butyl-4-hydroxybenzyl)-benzene; pentaerythritol tetrakis-3-(3,5-ditert.butyl-4-hydroxyphenyl)-propionate; n-octadecyl-3,5-ditert.butyl-4-hydroxyphenyl)-propionate; 4,4-methylene-bis-(2,6-ditert.butylphenol); 4,4-thiobis-(6-tert.butyl-o-cresol); 2,6-ditert.butylphenol; 6-(4-hydroxyphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine; di-n-octadecyl-3,5-ditert.butyl-4-hydroxybenzyl phosphonates; 2-(n-octylthio)-ethyl-3,5-ditert.butyl-4-hydroxybenzoate; and sorbitol hexa-[3-(3,5-ditert.butyl-4-hydroxyphenyl)-propionate].

Suitable photostabilizers are, for example, those marketed under the name of Tinuvin® (manufacturer: Ciba Geigy).

Other additives may be incorporated in the adhesives according to the invention in order to vary certain properties. These other additives include, for example, dyes, such as titanium dioxide, fillers, such as talcum, clay and the like. The adhesives according to the invention may optionally contain small quantities of thermoplastic polymers or copolymers, for example ethylene/vinyl acetate (EVA), ethylene/acrylic acid, ethylene/methacrylate and ethylene/n-butyl acrylate copolymers which optionally provide the adhesive with additional flexibility, toughness and strength. It is also possible - and preferred in accordance with the invention - to add certain hydrophilic polymers, for example polyvinyl alcohol, hydroxyethyl cellulose, hydroxypropyl cellulose, polyvinyl methyl ether, polyethylene oxide, polyvinyl pyrrolidone, polyethyl oxazolines or starch or cellulose esters, more particularly the acetates with a degree of substitution of less than 2.5, which increase the wettability of the adhesives.

In addition, the adhesives according to the invention may contain tackifier resins. Suitable tackifier resins are, for example, hydrocarbon resins, more particularly C5 or C9 resins or C9 resins modified with C5

resins. Also suitable for use as tackifier resins are resins based on pure hydrocarbon monomers, for example resins obtainable from the polymerization of mixtures of styrene,  $\alpha$ -methyl styrene and vinyl toluene. The hydrocarbon resins mentioned may be partly hydrogenated or fully  
5 hydrogenated.

The tackifier resins may also be selected from natural resins, such as gum rosin obtainable, for example, from trees, or tall oil resin which accumulates in papermaking. The natural resins may be used as tackifier resins in the form mentioned above although they may also be used after  
10 esterification with corresponding polyhydric alcohols as pentaerythritol esters, glycerol esters, diethylene glycol esters, triethylene glycol esters or methyl esters.

Other suitable tackifier resins are the polyterpene resins. Terpenes accumulate in the separation of resin acids from their natural solvents and  
15 may be polymerized to form polyterpene resins. The terpene/phenol resins obtainable from polyterpene resins by phenol modification are also suitable for use as tackifier resins.

The present invention also relates to a process for the production of a polyurethane composition as claimed in any of claims 1 to 7, in which at  
20 least two components A and B are reacted with one another,

- (g) at least one polyurethane prepolymer obtainable by reacting at least one polyol component with at least two at least difunctional different isocyanates being used as component A and
- (h) an at least difunctional hardener containing at least two isocyanate-  
25 reactive functional groups per molecule being used as component B, and the ratio of isocyanate groups to isocyanate-reactive functional groups being greater than about 0.75:1 and smaller than about 1.15:1.

The present invention also relates to the use of a polyurethane composition according to the invention as a contact adhesive, more  
30 particularly as a contact adhesive in the packaging industry for the

laminated coating of substrates, for example paperboard articles, for the coating of paper, for example for the production of self-adhesive labels, for the coating of films and laminates, for example for the production of resealable packs, and as a laminating adhesive.

5           The present invention also relates to resealable packs which have been produced using a polyurethane composition according to the invention.

The following Examples are intended to illustrate the invention without limiting it in any way.

10

### **Examples**

List of the abbreviations used:

- DPG = dipropylene glycol
- PPG1 = polypropylene glycol, OH value ca. 109
- 15 PPG2 = polypropylene glycol, OH value ca. 250
- PPG3 = TMP-started polypropylene glycol, OH value ca. 256
- TDI = toluene diisocyanate (2,4-isomer)
- MDI = 4,4'-diphenyl methane diisocyanate
- PE1 = polyester based on isophthalic acid/phthalic acid/adipic acid/diethylene glycol/neopentyl glycol/dipropylene glycol in a
- 20 ratio by weight of about 3:2:50:30:5:20, OH value ca. 130
- PE2 = polyester based on isophthalic acid/phthalic acid/adipic acid/diethylene glycol/propylene glycol in a ratio by weight of about 30:10:20:30:10
- 25 NCO = isocyanate group content
- MR = mixing ratio
- LA = laminate adhesion
- SSA = sealing seam adhesion
- LDPE = polyethylene film of LDPE, thickness: ca. 30  $\mu$ m, a product of
- 30 M&W

PET<sub>12μ</sub> = polyethylene terephthalate film, thickness: ca. 12 μm, a product of Mitsubishi

PETP<sub>12μm</sub> = stretched polyethylene terephthalate film, printed, thickness: ca. 12 μm, a product of Mutsubishi

PE<sub>KO88</sub> = LLDPE/LDPE blend, thickness: ca. 70 μm, manufacturer: Mildenberger und Willing

For Examples 1 to 12, components A and B were prepared as described in the specification. Resin 1 is intended for comparison purposes.

The following components A were used.

Table 1: component A

Raw material	Percentages by weight in %		
	Resin 1	Resin 2	Resin 3
PE1	15	31	
PPG3			6
PPG1	15	33	62
PPG2	14	9.6	5.5
TDI	-----	24	24
MDI	56	2.4	2.5
NCO	17%	4.2%	4.8%

The following components B were used.

Table 2: component B

	Parts by weight		
Raw materials	Hardener 1	Hardener 2	Hardener 3
PE1	10	40	10
PE2	30	----	10
PPG1	----	40	30
PPG2	5	----	30
PPG3	----	10	----
DEG	----	----	20

Components A and B were mixed in the ratios shown below and applied to the correspondingly identified films. The laminates were tested after a curing time of about 14 days.

Table 3: test results

Lami nate No.	Laminate structure	PU composition	LA [N/15 mm]	LA [N/15 mm] after opening and closing 10 times
1.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 3, hardener 1, MR: 6:1	3.1 PET failure	0.2 Adhesive to PE
2.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 3, hardener 1, MR: 5:1	2.1 Adhesive to PE	0.2 Adhesive to PE
3.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 2, hardener 2, MR: 6:1	3.3 PET failure	0.2 Adhesive to PE
4.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 2, hardener 2, MR: 5:1	3.3 PET failure	0.2 Adhesive to PE
5.	PETP <sub>12μ</sub> /LDPE	Resin 2, hardener 2, MR: 4:1	2.0 Adhesive to both sides	1.0 Adhesive to both sides
6.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 3, hardener 1, MR: 6:1	2.2 Adhesive to PE	0.2 Adhesive to PE
7.	PETP <sub>12μ</sub> /LDPE	Resin 3, hardener 1, MR: 5:1	2.2 Adhesive to PE	0.2 Adhesive to PE
8.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 3, hardener 1, MR: 5:1	2.2 Adhesive to PE	0.2 Adhesive to PE
9.	PET <sub>12μ</sub> /LDPE	Resin 3, hardener 1, MR: 5:1	2.3 Adhesive to PE	0.2 Adhesive to PE
10.	PET <sub>12μ</sub> /PE <sub>KO88</sub>	Resin 2, hardener 2, MR: 6:1	3.5 Adhesive to PE	0.2 Adhesive to PE
11.	PET <sub>12μ</sub> /LDPE	Resin 2, hardener 2, MR: 6:1	3.2 Adhesive to PE	0.2 Adhesive to PE
12.	PET <sub>12μ</sub> /LDPE	Resin 1, hardener 3, MR: 100:70	12 PET elongation	-----



**CLAIMS**

1. A polyurethane composition obtainable by reacting two components A and B,
  - a) at least one polyurethane prepolymer A1 obtainable by reacting at  
5 least one polyol component with at least two at least difunctional different isocyanates being used as component A and
  - b) an at least difunctional hardener containing at least two isocyanate-reactive functional groups per molecule being used as component B, and the ratio of isocyanate groups to isocyanate-reactive functional groups  
10 being greater than 0.75:1 and smaller than 1.15:1.
2. A polyurethane composition as claimed in claim 1, characterized in that the ratio of isocyanate groups to isocyanate-reactive functional groups is more than 1 to 1.15:1.
3. A polyurethane composition as claimed in claim 1 or 2,  
15 characterized in that TDI and MDI are used as the at least two difunctional different isocyanates.
4. A polyurethane composition as claimed in any of claims 1 to 3, characterized in that the polyol component has a functionality of 2.0 to 2.3.
5. A polyurethane composition as claimed in any of claims 1 to 3,  
20 characterized in that the polyol component contains at least one polyester and at least one polyether.
6. A polyurethane composition as claimed in any of claims 1 to 3, characterized in that the polyol component contains at least one polyester, at least one difunctional polyether and at least one trifunctional polyether.
- 25 7. A polyurethane composition as claimed in any of claims 1 to 3, characterized in that component A has an NCO group content of 2 to 8% by weight before components A and B are mixed.
8. A process for the production of the polyurethane composition claimed in any of claims 1 to 7, in which at least two components A and B  
30 are reacted with one another,

- (a) at least one polyurethane prepolymer obtainable by reacting at least one polyol component with at least two at least difunctional different isocyanates being used as component A and
  - (b) an at least difunctional hardener containing at least two isocyanate-reactive functional groups per molecule being used as component B, and the ratio of isocyanate groups to isocyanate-reactive functional groups being greater than about 0.75:1 and smaller than about 1.15:1.
- 5
9. The use of the polyurethane composition claimed in any of claims 1 to 7 or produced by the process claimed in claim 8 as a contact adhesive.
- 10
10. A resealable pack produced using the polyurethane composition claimed in any of claims 1 to 7 or produced by the process claimed in claim 8.

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(54) Bezeichnung: HAFTKLEBRIGE POLYURETHANZUSAMMENSETZUNG MIT EINEM NIEDRIGEN MONOMERGE-  
HALT

(57) Abstract: The invention relates to a polyurethane composition with the properties of a pressure-sensitive adhesive, to a method for its production and to its use as pressure-sensitive adhesive. The aim of the invention is to provide an optimized adhesive that has good adhesive properties even when the adhesive link has been repeatedly released and joined again and with a reduced migration of noxious components. To this end, the invention provides a polyurethane composition that is obtained by reacting two components A and B, wherein a) at least one polyurethane prepolymer A1 is used as component the A, said prepolymer having been obtained by reacting at least one polyol component with at least two bifunctional different isocyanates, and b) at least one bifunctional hardener as the component B, said hardener having per molecule at least two functional groups that are reactive to isocyanate groups. The ratio of isocyanate groups to functional groups that are reactive to isocyanate groups should be greater than 0.75 and lower than 1.15.

(57) Zusammenfassung: Die Erfindung betrifft eine Polyurethanzusammensetzung mit haftklebrigen Eigenschaften, ein Verfahren zu deren Herstellung sowie ihre Verwendung als Haftklebstoff. Zur Optimierung des Klebstoffes im Hinblick auf die Haftung nach mehrfachem Öffnen und wieder Zusammenfügen der Klebeverbindung sowie auf die Migration schädlicher Komponenten wird eine Polyurethanzusammensetzung vorgeschlagen, die erhältlich ist durch Umsetzung zweier Komponenten A und B, wobei a) als Komponente A mindestens ein Polyurethan Präpolymeres A1 eingesetzt wird, das durch Umsetzung mindestens einer Polyolkomponente mit mindestens zwei mindestens difunktionellen unterschiedlichen Isocyanaten erhältlich ist und b) als Komponente B ein mindestens difunktioneller Härter eingesetzt wird, der pro Molekül mindestens zwei gegenüber Isocyanatgruppen reaktionsfähige funktionelle Gruppe aufweist, wobei das Verhältnis von Isocyanatgruppen zu gegenüber Isocyanatgruppen reaktionsfähigen funktionellen Gruppen grösser als 0,75 und kleiner als 1,15 ist.

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